DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS
George K. Burgess, Director

MEASUREMENT OF THE DEGREE OF SIZING OF PAPER

By F. T. CARSON

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BY

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Bureau of Standards

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ABSTRACT

The attempt to obtain a satisfactory means of measuring the degree of sizing of paper or its resistance to permeation by aqueous liquids has resulted in the proposal of no less than 38 sizing tests. For the first time in a single publication these have been described, critically discussed, and the most important ones compared experimentally. Stress is laid on the essential difference in the capillary flow in the direction of the length of the fibers and in the direction normal to their length, and a recommendation made that degree of surface sizing and degree of internal sizing be recognized as separate properties. In general, the various tests are entirely contradictory in their results. This is found to be due largely to the effects of selective adsorption from solution and of an extraneous resistivity. Tests of rate of penetration of water are considered the most logical and the type most indicative of degree of internal sizing. Two methods of this type have been developed at the Bureau of Standards—the curl method and a new test using a dry indicator on one surface of the paper.

These methods were compared experimentally on 63 samples of paper with the Stöckigt, the electrolytic, and the ink flotation methods. The curl and indicator methods corroborated each other and gave the most consistent and reasonable results. The Stöckigt method is fairly consistent, the electrolytic confirms these tests on some papers, but, on the whole, is not reliable, and the ink flotation was found too inconsistent for serious consideration.

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I. INTRODUCTION

Paper is "sized," as the process is called, by incorporating water-resistant materials in it so that the paper resists wetting. Paper which is not sized, such as blotting paper and filter paper, is very absorbent. The oldest means of sizing consisted in treating the paper with such materials as glue and starch in order to make them take writing ink smoothly. This corresponds to the tub sizing of present practice. A later method of sizing which now predominates is to treat the constituent fibers before the sheet is fabricated. This is done by coating the fiber surfaces with a water-resistant material, such as rosin, during the preparation of the fibers for the process of forming the sheet. This method is called engine sizing, because it is usually carried out in the beating engine.

The control of a process as complicated in its mechanism as the sizing of paper is extremely difficult and very uncertain without adequate means of measuring the quality which the process imparts to the finished paper. Converting and other manufacturing operations related to the making of paper may be greatly facilitated by a satisfactory means of measuring this property of paper. In addition to its value to the manufacturer and converter, such a testing method would be very useful to the larger consumers of paper, many of whom maintain testing laboratories.

The viewpoint of the consumer of paper has been somewhat neglected in the development of testing methods. There is a growing appreciation of adequate testing methods in the selection of paper for a particular use. The consumer's requirements of a test may be more exacting than are those of the manufacturer. A sizing test to benefit the user must indicate the quality of the paper regardless of its previous history. A test suitable for a given kind of paper made always under the same conditions may be misleading when applied to papers of different kinds and from different sources.

Recent research has aided greatly in understanding something of the complicated phenomena involved in rosin sizing, but most of this work has dealt with ideal rather than actual conditions. There is still a considerable gap between the deductions drawn from experiments carried out under selected conditions and their application under the various conditions obtaining in actual mill operation. More experimentation is desirable in applying general deductions to specific sets of conditions as well as in studying the fundamental character of the process. In making a study of this nature an adequate measure of the degree of sizing of paper is essential. The study of engine sizing has been greatly hampered by the inadequacy of methods of testing this property of paper. Other paper-making processes, such as tub sizing and coating, can be better controlled

and more economically effected, with a resulting product which is better and more uniform, when such processes are properly correlated with the degree of sizing of the paper involved.

In attempting to determine the resistance offered by paper to the absorption of water and aqueous solutions, a property variously designated as degree of sizing, sizing quality, size fastness, or simply sizing, one may choose from nearly 40 testing methods which have been proposed for measuring this property. The outstanding feature is disagreement in the results obtained by the different methods. The choice of a sizing test is consequently a formidable task.

Crude tests have long been employed for judging the degree of sizing of paper. It is easy to tell whether paper is well sized or poorly sized. The attitude is often taken that this is sufficient for all practical purposes, and that the method of measurement is of little consequence. But it is probable that much of the confusion and conflicting opinions which exist relative to sizing are traceable to the discordant methods used in testing the degree of sizing of paper. The purpose of this publication is to point out the chief elements of disagreement and to present the results of a comparative experimental study of several of the most promising methods.

II. AVAILABLE TESTS FOR DEGREE OF SIZING

The number of methods which have been proposed for determining the degree of sizing of paper is surprisingly large. Some of these have long been in use, others have been only recently proposed. A number of writers have described and treated several of these methods together, but there does not appear to have been an attempt to treat in one publication all the methods described in the literature. In this publication, for the first time, an attempt has been made to describe all such methods. Thirty-eight methods and modifications of methods are described and classified in four groups according to type.[1] Figure 1 shows in compact form these methods and their classification. Each type is discussed critically, and the outstanding methods of each group are compared by means of experimental data.

1. Group A.—TESTS WITH INK

(*a*) Method of Written Characters.—This method, which is no doubt the most ancient test of paper, consists in writing rather heavily upon paper with writing ink, allowing the ink to dry and observing whether or not written characters are clear cut; that is, whether or not the ink has dried without any tendency to spread or "feather." The reverse side of the sheet is also observed in order

[1] The writer is indebted to Dr. V. H. Gottschalk, of the Bureau of Efficiency, for assistance in collecting these various methods and for the translation of original sources.

to determine whether or not the ink has dried without staining through.

(*b*) Method of Herzberg (17).[2]—Using various commercial inks, lines of varying widths are drawn on the paper to be tested by means of a ruling pen, care being taken that the amount of ink in the pen, the pressure, inclination, and rate of movement of the pen are uniform in all tests. The minimum width of line which permits the ink to penetrate through the sheet is called the critical width of line, and this critical width in millimeters is designated as a numerical expression of the degree of sizing of the paper.

(*c*) Method of Denoël (14).—This method carries out Herzberg's suggestion that an apparatus could be designed to bring about absolute uniformity in the carrying out of a test with ink lines.

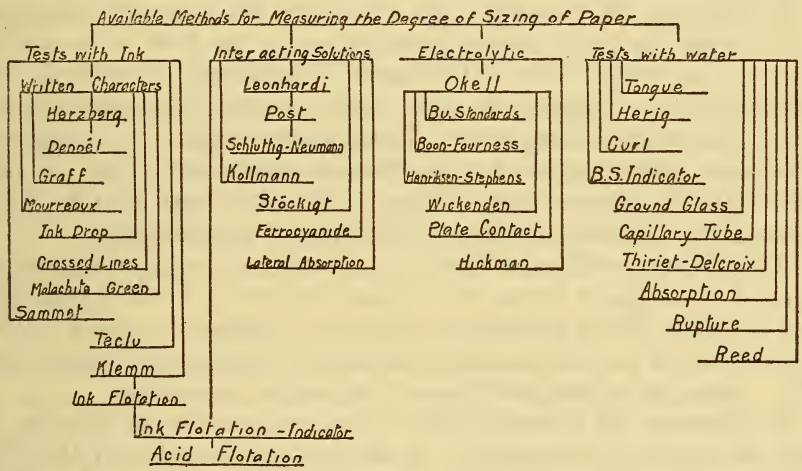

Fig. 1.—*Classification of sizing test methods*

Lines are drawn by means of a mechanically operated gang pen having tip openings varying in width from ¼ to 2¼ millimeters. The degree of sizing is expressed numerically as a function of the minimum width of line producing transudation of ink.

(*d*) Method of Graff (47).—It is proposed that a line of definite width be drawn in a uniform manner with a standard ink on the paper to be tested, a specially designed drawing instrument being employed for the purpose. By means of a microscope fitted with a micrometer scale the width of the line is measured as soon as the line is laid down and again after the ink is dry, the percentage increase thus measured being recorded as an indication of the degree of sizing of the paper.

[2] The figures given in parentheses here and throughout the text relate to the reference numbers in the bibliography at the end of this paper.

(*e*) Method of Mourreaux (31).—Three strokes of varying widths are drawn on a sheet of paper. These ink lines are watched while drying, and as any part of a line becomes dry the time of drying is noted and two pencil marks are made to indicate the limits of this portion. When all the lines are dry, the sheet is reversed and any part of a line which has penetrated through is noted. The time of drying of this portion of a line is recorded as a measure of the degree of sizing of the paper.

(*f*) Ink-Drop Test (41).—Allow one drop of ink to fall upon each of the sheets of paper to be compared; at first the drop is spherical, but after awhile it becomes slightly flattened and covers a larger area. With well-sized papers the drop will retain its spherical form for a considerable period.

(*g*) Method of Crossed Lines.—Heavy ink lines are drawn on one side of the paper under examination in the form of a double cross. The reverse side of the paper is examined at intervals for transuded ink. Staining through usually occurs first under the intersections of the crossed lines. Transudation within 5 minutes indicates slack sizing; within 5 to 10 minutes, satisfactory sizing; in not less than 10 minutes, hard sizing. The sheet may also be torn through the ink lines to observe the depth of penetration.

(*h*) Malachite-Green Test.—A solution of malachite green is applied to the paper by means of a pen, preferably a ruling pen, and any tendency of the solution to spread or "feather" is noted. The reverse side of the sheet is also examined for staining through of the dye. Lines of varying widths may be used to advantage.

(*i*) Method of Sammet (37).—The test consists in drawing a strip of paper over the surface of an iron tannate ink and allowing it to drain and dry naturally. Upon examining this inked surface with a magnifying glass it will be found that a well-sized paper will show no indication of the fiber having absorbed the ink, and the entire surface will be uniformly and lightly colored. In paper not so well sized the fibers absorb the ink in blotches, and a mottled appearance results. By repeating the test on erased surfaces the degree of uniformity of sizing throughout the sheet is determined.

(*j*) Method of Teclu (48).—Drops of a 0.2 per cent solution of a blue dye (referred to as crystallized "Neublau") is delivered from a burette, the tip of which has a 2-millimeter opening and is placed 5 centimeters above the paper to be tested. When dry, the paper is cut through each of the stained places and examined under a specially constructed microscope to determine the depth to which the solution has penetrated into the paper. The difference between this depth of penetration and the thickness of the sheet is expressed as a percentage of the thickness of the sheet and recorded as a numerical expression of the degree of sizing of the paper.

(*k*) Method of Klemm (23).—Specimens of paper are allowed to float on ink for varying periods of time (5, 10, 20, etc., minutes). They are then removed, the excess ink is brushed off on the side of the vessel, and the specimens are pressed between pieces of blotting paper. The specimen on which the first transudation of ink is observed and the succeeding specimens up to complete saturation afford a continuous record of the resistance of the paper to the penetration of ink.

(*l*) Ink-Flotation Test.—A sizing test somewhat similar to the method of Klemm (perhaps an adaptation of it) has long been used in this country and to-day enjoys the prestige of custom and precedent. Specimens of paper are floated on the surface of ink and kept continuously under observation until transudation of ink is detected on the upper side. The time interval required for the staining through of the ink is considered a measure of the degree of sizing of the paper.

2. Group B.—TESTS USING INTERACTING SOLUTIONS

(*a*) Method of Leonhardi (28).—A neutral solution of iron chloride, containing 1.531 per cent iron, is applied to paper by means of a ruling pen which draws a line 1 millimeter wide. After the paper has been dried a small amount of an ethereal solution of tannic acid is applied to the reverse side. If the paper is not sized, a dark stain will appear where the iron choloride solution has passed through the sheet.

(*b*) Method of Post (17).—A small drop (0.03 g) of an iron chloride solution, containing 1.531 per cent iron, is allowed to fall from a height of 10 centimeters upon the paper to be tested. The drop is left on the paper for a period of seconds equal in number to the weight of the paper in grams per square meter, when it is quickly removed with filter paper. The reverse side of the sheet is then moistened with a dilute aqueous solution of tannic acid, the excess of which is immediately removed with a blotter. The depth of color resulting is considered a measure of the degree of sizing of the paper.

(*c*) Method of Schluttig and Neumann (39).—The paper is supported so that its surface makes an angle of 60° with the horizontal. From a trough, supported at an angle of 45° to the surface of the paper, a solution of ferric chloride, containing 1 per cent iron, 1 per cent gum arabic, and 0.2 per cent phenol, is allowed to run down the paper. Three parallel lines of liquid 3 centimeters apart are laid down in this manner. Similarly, three paths of a 1 per cent aqueous solution of tannic acid containing 0.2 per cent phenol are laid down on the opposite side of the sheet, but at right angles to the first three. Thus, at nine points the two solutions may meet and interact first to produce a more or less dark stain. The depth of color

produced within a given period of time is regarded as an indication of degree of sizing.

(*d*) Method of Kollmann (26).—The paper is treated upon one side with a solution of phenolphthalein and upon the other with a solution of sodium hydroxide. The time from the application of the solutions until the appearance of the red color which results from their meeting is considered a measure of degree of sizing.

(*e*) Method of Stöckigt (45).—A specimen of paper is floated on a 2 per cent solution of ammonium thiocyanate. The upper surface is lightly dabbed with a brush wetted with a 1 per cent solution of ferric chloride until red specks of iron thiocyanate appear all over the surface of the sheet. The experimental datum of the test is the time from the contact of the paper with the ammonium thiocyanate until the appearance of the red specks on the upper surface. A useful modification of this method consists in applying the ferric chloride at frequent intervals with a pen or fine-tipped brush, always in a new place, until the red coloration develops immediately.

(*f*) Ferrocyanide Test (15).—Float a piece of paper about 2 inches square on the surface of a 5 per cent solution of potassium ferrocyanide and note the time. Then test the upper surface of the piece of paper from time to time by stroking (across the machine direction) with a small camel's-hair brush moistened with a solution of ferric chloride (5 to 10 per cent). When the ferrocyanide has soaked up through the paper sufficiently to come in contact with the ferric chloride, it will react the moment the latter is applied and give a blue color. The penetration is then considered complete, the time is again noted, and the length of time since the paper was laid upon the surface of the solution is taken as a measure of its resistance to penetration. In stroking the paper with the camel's-hair brush, take care to select a place on the paper which has not previously been wet with the ferric-chloride solution. Report the results to the nearest minute, or, if the time is very short, in seconds.

(*g*) Lateral Absorption Test.[3]—Two interacting solutions, such as ferric chloride and ammonium thiocyanate, are held in two drawing pens separated by a small interval. By means of this double pen two parallel lines are drawn very close together. The time required for the two solutions to run together and produce a color is a measure of the lateral absorption exhibited by the paper toward the solutions.

(*h*) Ink Flotation-Indicator Test.—An extension of the ink-flotation method takes advantage of the presence of acid in writing inks. A suitable indicator, such as methyl orange or congo red, is applied to the upper surface of a sample of paper floating on ink. The time until the indicator shows the presence of transuded acid is regarded as a measure of degree of sizing.

[3] This method, originating at the Bureau of Standards, has not previously been published.

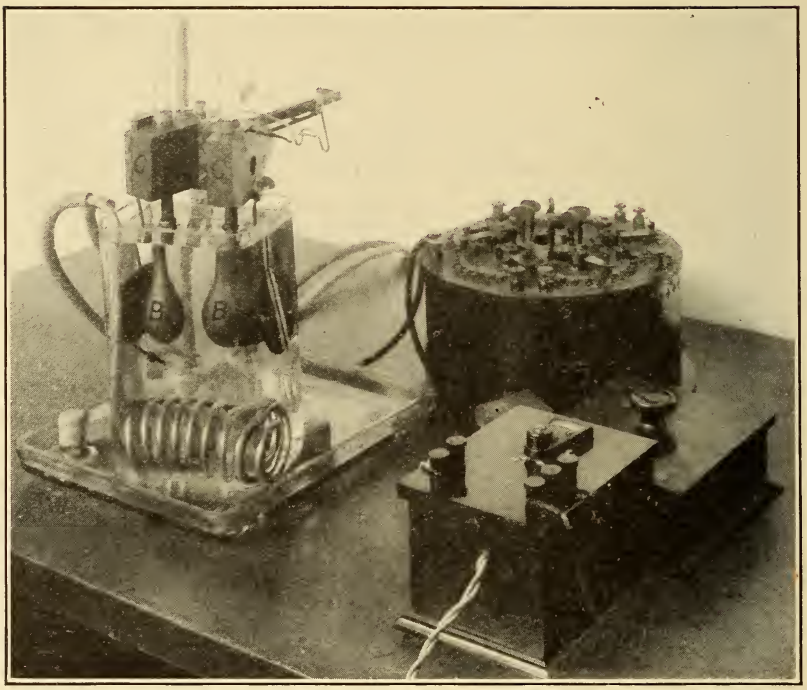

FIG. 2.—*Bureau of Standards' electrolytic sizing tester*

(*i*) Acid-Flotation Test.—The next logical step in the evolution of flotation methods is the elimination of the ink and the substitution of a colorless solution of like acidity. Specimens of paper are floated upon such an acid solution, and the time of transudation of acid, as determined by the use of suitable indicators, is recorded as a measure of the degree of sizing of the paper.

3. Group C.—TESTS USING THE PRINCIPLE OF ELECTROLYTIC CONDUCTIVITY

(*a*) Method of Okell (32).—An old idea was given a new application when the Kohlrausch method of conductivity measurement was cleverly adapted to the problem of the measurement of the degree of sizing of paper. According to the proposal of Okell, the paper to be tested is interposed between the electrodes of a specially constructed electrolytic cell having controlled means of bringing the electrolyte into contact with the paper. As the solution of electrolyte penetrates the paper partition from both sides the decreasing resistance (or increasing conductance) is measured by means of a Wheatstone bridge. By plotting the resistance (or conductance) against time a continuous record is obtained, and, assuming the rate of increase of conductance to be proportional to the rate of increase of permeation, the data are interpreted in terms of degree of sizing.

(*b*) Bureau of Standards Electrolytic Method (3).—A photograph of this modification is shown in Figure 2. The cell *C* is made up of two parts, each containing a large platinized electrode. The two halves are mounted on pivoted lever arms, so that the paper to be tested is held securely between the two halves by clamping together the opposite ends of the levers. The electrolyte is contained in the two bags *B*, immersed in a constant temperature water bath which may be maintained at any required temperature. The cell is filled by means of pressure on the bags through a system of levers. This divided cell is placed in the Wheatstone bridge in the position of the unknown resistance. Its normal resistance without a paper partition is determined and balanced so that no current passes through the sensitive alternating-current galvanometer which is used instead of the telephone receiver employed by Okell. The paper to be tested is now clamped between the two halves of the cell and the electrolyte admitted. The initial resistance of the cell is very high, but decreases at a rate depending, in part, upon how well the paper is sized. As the resistance decreases the slide wire is used to hold the galvanometer reading at zero. The slide-wire readings are plotted against time on coordinate paper carried on a recording drum (not shown in the photograph), or a definite reading on the slide wire is chosen as an end point. In the latter case the time is determined from the contact of the electrolyte

with the paper until the galvanometer reads zero for the slide-wire ratio which has been chosen as the end point.

(*c*) Method of Boon and Fourness (2).—In order to obviate the use of a sensitive galvanometer or telephone receiver, the method of Okell is modified so as to substitute a series circuit containing a milliammeter for the Wheatstone bridge. A constant temperature is maintained thermostatically. An arbitrary end point is chosen which is four-fifths the normal conductance of the circuit when operated with no paper in the cell. A commercial instrument of this type was used in the comparative tests to be described in this publication.

(*d*) Method of Henriksen, Zbyshevski, and Stephens (43).—This modification consists chiefly of the form of cell used. The containers for the electrolyte are made integral with the cell, the whole being mounted on a horizontal axis, so that the electrolyte is brought into contact with the paper merely by turning the cell upside down. The cell is connected in series with an ammeter.

(*e*) Method of Wickenden.—In this modification the electrolyte is applied to the paper from wicks held in contact with the two surfaces of the paper by means of rollers. The lower ends of the wicks dip into the solution of electrolyte. Otherwise the test is carried out in a manner similar to that of Okell.

(*f*) Plate-contact Method.—A crude modification of the electrolytic principle employs a metal plate upon which the paper is placed. Electrolyte is poured on the paper and an electrode placed in it. When the electrolyte passes through the paper and touches the plate, the circuit is completed through an electric bell and source of current, whereupon the bell rings and the time is recorded from the contact of electrolyte with the paper until the signal is heard.

(*g*) Method of Hickman.[4]—A cell somewhat like Okell's is used, one chamber being provided with a platinized electrode and capable of being filled with an electrolyte and the other capable of being filled with mercury having electrical contact with a circuit. The circuit is made up of the cell, a sensitive direct-current galvanometer previously calibrated against known resistances in the circuit, a known high resistance to protect the galvanometer, and a source of direct current. The resistance per unit area of the paper to be tested is first determined. The paper is then placed in the cell and the mercury and electrolyte admitted to opposite sides of the specimen. The resistance is measured and plotted against time as the electrolyte penetrates the paper from one side. In the Okell method the curve is a record of the meeting of the electrolyte, and no effect is observed until the electrolyte has met at some point. In the Hickman method

[4] Suggested to the writer by C. N. Hickman, formerly of the Bureau of Standards, as a means of eliminating many of the objectionable features found in the Okell method. (See, also, footnote 3, p. 710.)

the changing resistance is observed from the instant the electrolyte touches the paper, and the whole test is over in the time the Okell test would be getting under way. This method appears to overcome the chief objection against the Okell method in that the resistance of the air in the paper is accounted for at all times; but it requires rather elaborate apparatus, and owing to its rapidity a test would be difficult except on hard-sized or very heavy papers. Hence, it seemed preferable to turn the attention to the development of simpler methods which gave promise of accomplishing the same purpose.

4. Group D.—TESTS WITH WATER

(*a*) Absorption Test.—The usual method of determining the absorptivity of porous substances is to immerse the material in the liquid concerned and measure the amount and rate of absorption by weighing at definite time intervals. This method is properly included among sizing tests, for, although it has not been found practicable for the usual weights of paper, it is of value in testing the class of paper known as boards.

(*b*) Tongue Test.—This test, the one most familiar to the practical millman, is made by touching the tongue to the surface of the paper and looking at the paper by both reflected light and transmitted light in order to judge the rapidity with which the moisture sinks into the sheet. If it is absorbed rapidly, the paper is considered poorly sized.

(*c*) Method of Herig (16).—Finely powdered aniline dye, preferably mahogany red or methyl violet, is placed in a depression made by cutting some design from cardboard and pasting this cardboard upon another piece of the same material. The paper to be tested is laid over the aniline dye and pressed down gently, so that some of the dye clings to the surface over the area of the figure. The paper is then floated on water with the dye uppermost. When transudation of the water occurs, the shape of the figure stands out as a result of the deepening of the color of the dye. The time of transudation of water is recorded as a test of relative permeability of the paper.

(*d*) Curl Method (3) (6).—When a small piece of paper is floated on water, it curls up as a result of the wetting and consequent expansion of the under side. In a short time it attains a maximum degree of curling and then begins to uncurl as a result of expansion setting in on the upper side of the sheet as the water penetrates beyond the median plane. The time from the contact of the paper with the water until the instant when the specimen begins to uncurl is considered a measure of the relative degree of sizing within the sheet for papers of the same thickness, tested under the same conditions of temperature and relative humidity. When it is necessary to test papers of different thicknesses, the quotient obtained by dividing

the time by the square of the thickness in each case is an expression of the relative degree of sizing within the sheet.

The test is made preferably with an apparatus such as that shown in Figure 3. The specimen *S* is held in a definite position on a float *F*, having an aperture through which the water presents a small restricted surface convex upward. The part of the specimen lying over this aperture is wetted on the under side. The pointed part remains dry and serves as a pointer to magnify the movement due to the curling. This pointer is viewed against a background of small black dots on a white field, which facilitates determining the instant at which it begins to retreat. The whole mechanism is controlled by an operating lever, the initial depression of which brings the specimen in contact with the water and starts a stop watch. A second depression of the lever at the instant the specimen starts to uncurl arrests the stop watch. The time is recorded. On raising the lever to the vertical position the stop watch is set to zero, the transparent hood is thrown back, and the specimen is lifted from the water. When a new specimen is put in position on the float, all is in readiness for another test.

(*e*) Bureau of Standards Dry-Indicator Method (7).—The accidental observation that grains of sugar on the surface of paper give an indication of the presence of transuded moisture by melting down into droplets long before the presence of water can be detected by other simple means has led to the development of a new method at the Bureau of Standards. Sugar, at first used alone, was supplemented to great advantage by adding small amounts of dyes. Powdered sugar and one or more water-soluble dyes are mixed in such proportion (approximately 50 parts of sugar to 1 part of dye) that the mixture shows very little color. The mixture is applied through a sieve to the paper being tested. The specimen is then floated on a vessel of water at a definite temperature and the time determined until the characteristic color of the dye begins to appear in the mixture as a result of wetting by transuded moisture. This time interval is then interpreted in the same manner as in the curl method, either as a measure of the relative degree of sizing of papers of the same thickness or by accounting for the effect of thickness in the manner described under the description of the curl method.

This method is susceptible of a number of modifications. At first methyl blue was employed as the dye constituent. Later fuchsine, methyl green, and a soluble yellow were used in three separate mixtures for the sake of the color contrast which helps in determining the end point. A procedure which gives excellent results is the following:

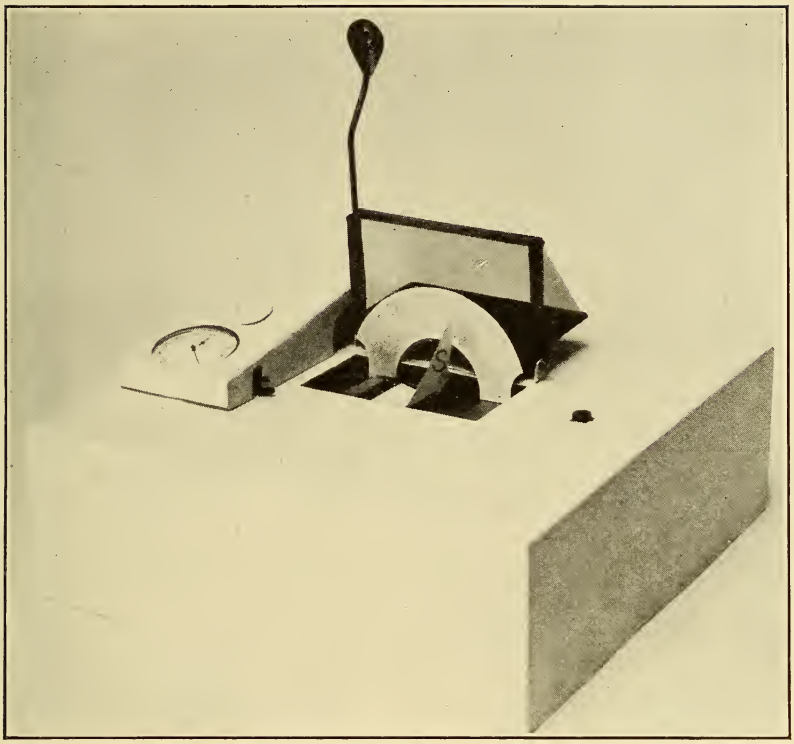

FIG. 3.—*Curl sizing tester*

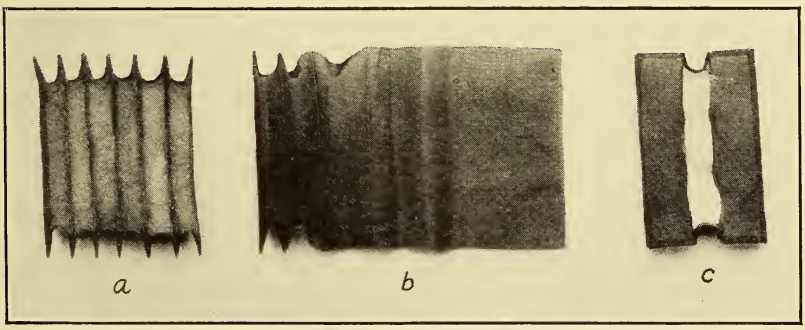

FIG. 4.—*Bureau of Standards' dry indicator sizing test*

(*a*) 6-compartment sieve for three sugar-dye mixtures and three sugar-pigment mixtures; (*b*) method of forming fluted sieve; (*c*) single-compartment sieve with sugar-dye mixture in center and sugar-pigment reference mixture on either side

Three mixtures are prepared of powdered sugar and small amounts of finely divided dyes in the approximate ratio 50:1. The first contains methyl green, the second pontacyl scarlet, and the third national wool yellow. Three other mixtures are made, using pigments insoluble in water instead of the dyes, each of the latter three mixtures being made up to match in color one of the first three. A fluted sieve (fig. 4, *a*) is made of wire screen (about 80 mesh) such as that used on a Fourdrinier paper machine. The manner of construction is illustrated by *b* of Figure 4. Into every other trough one of the sugar-dye mixtures is placed. Each sugar-pigment mixture is then placed in one of the three remaining troughs, so that it is adjacent to the sugar-dye mixture of the same color. A test specimen is cut about 3 inches square and the edges folded over to prevent curling. The sieve is dropped on this specimen from a height of about a quarter of an inch, as a result of which the indicator mixtures are laid down close to one another in parallel lines. On floating the specimen, water penetrates through and is taken up by the sugar and transferred to the particles of dye scattered through it. The colors deepen markedly and rapidly and, in contrast with the reference mixtures, stand out prominently. The end point is when one is certain that the colors have begun to develop. The end point is influenced somewhat by the solubility of the dyes. When not in use, the indicator mixtures should be kept in a desiccator. It is well to prepare fresh mixtures frequently. In order to get comparative results over a period of time, all tests should be made under the same conditions of temperature and relative humidity.

The procedure which, perhaps, best combines simplicity with a sharp end point employs one of the sugar-dye mixtures flanked on either side by its reference mixture of sugar and an insoluble pigment. In this case only one trough in the sieve is required. This procedure is illustrated by *c* of Figure 4.

(*f*) Bureau of Standards Ground-Glass Method (5) (7).—The paper to be tested is folded box shape or sealed to a cylinder, and the recepatcle thus formed is partially filled with water and set on a ground-glass surface placed over a black background. When water goes through the sheet and touches the ground surface, the glass is made more transparent at that point, and on lifting the receptacle at intervals dark patches are seen. The time of transudation is a measure of the relative permeability of the paper to water.

(*g*) Capillary-Tube Method.[5]—A capillary tube ending in a relatively wide mouth is filled to a certain mark with water. A specimen of the paper to be tested is arranged so as to be brought into contact with the mouth of the capillary tube when desired. The image of the part of the tube near the mark is projected onto a screen

[5] See footnote 3, p. 710.

which has a scale. The rate of retreat of the meniscus is the experimental datum for obtaining the rate of absorption. The principal objection to the method is the fact that the paper expands and buckles on becoming wet and causes displacement of liquid not truly indicative of absorption.

(*h*) Method of Thiriet and Delcroix (50).—From the meager description of this method it appears to be similar to Klemm's method of testing bibulous paper by suspending strips dipping into a liquid and noting the height the liquid rises in a given time. The liquid employed in this case is water. It is applicable only to papers which are not well sized.

(*i*) Rupture Test.—A strip of paper is suspended in a horizontal plane between two jaws, one of which is movable and under a definite small load. A vessel filled to overflowing with water is then brought up underneath until the water touches the paper on the under side. The time from contact of the water until the strip ruptures under the small stress is regarded as a measure of the degree of impermeability of the paper.

(*j*) Method of Reed (35).—In another type of rupture test one side of a specimen of paper is left in contact with water for a definite period of time, after which a bursting test is made and compared with the original bursting strength of the dry paper. The residual bursting strength expressed as a percentage of the original bursting strength is considered a measure of the residual serviceability of the material, but may also be considered an indication of its resistance to wetting.

III. TYPES OF DEGREE OF SIZING

1. NOMENCLATURE AND DEFINITIONS

The term "degree of sizing" and its synonyms, such as sizing quality, size fastness, and sizing, have commonly been applied to the resistance which paper offers to the absorption of aqueous solutions, but the terms have been used very loosely and never adequately defined. A reason for this looseness of definition appears in the fact that more than one kind of degree of sizing must be recognized even when restricted to the relation of paper to aqueous solutions. A point which has been overlooked in the development of sizing tests is the lack of homogeneity of paper in its relation to degree of sizing. In the consideration of the strength of paper it is universally recognized that this property is characteristically different in the two principal directions of the sheet. In noting the physical behavior of paper when it becomes wet it is observed that not only is the expansion different in the two lateral directions, but, whereas the lateral expansion is usually not more than 2 or 3 per cent, the expansion in the direction of the thickness is often as great as 50 per cent. The

structure of paper is such that most of the fibers lie in, or nearly in, the plane of the paper. Capillary flow along the length of the fibers appears to behave in a somewhat different manner than such flow through the interstices in a general direction normal to the length of the fibers. It is not surprising, therefore, that paper is found to exhibit different degrees of hindrance to the absorption of an aqueous solution, depending upon whether the absorption is judged by the rate of penetration of the liquid or by the tendency of a line drawn on the surface to increase in breadth before drying. Originally tests were directed exclusively toward determining the behavior of paper toward writing inks. In the absence of a suitable means of measuring and expressing numerically the resistance of paper to the spreading of ink the attempt was made to supply this deficiency by a test of the time required for the ink to stain through the sheet. Methods employing interacting solutions applied to opposite sides of the sheet have been proposed solely for the purpose of making the end point more definite. Many methods have been developed with this purpose in view—all on the assumption that the tendency of the ink to spread on the surface is proportional to and measured by the rapidity of penetration of the aqueous solutions used in the test. The fallacy of this assumption has been attested by numerous observations and comparative tests. Papers of the same type and intended as duplicate samples have been found to grade in different orders by the two types of tests. Selective adsorption which will be more fully discussed further along in this article introduces another complication which renders impossible any clear-cut, specific definition of degree of sizing. Klemm (23) has already observed that there is no hope of expressing the resistance of paper to the penetration of liquids by a simple numerical value. One may go a step further and state that there is no hope of expressing the resistance of paper to the absorption of aqueous solutions by a simple numerical value. It seems desirable to recognize two fundamental types of degree of sizing, and it is urged that "degree of surface sizing" and "degree of internal sizing" or their equivalents be recognized.

These two types of degree of sizing are not to be confused with the usual means of obtaining them. Internal sizing is usually effected by the process of engine sizing; that is, by adding water resistant materials, such as rosin, to the beater and incorporating such materials in fairly uniform distribution throughout the sheet. Surface sizing, on the other hand, is ordinarily obtained by applying the sizing material to the surface of the machine-finished paper; but many writing papers are engine sized only, and many papers designed to resist the penetration of water and its solutions are given a surface sizing. The type of sizing test to be used in a given case should be determined by the use for which the paper is intended.

2. DEGREE OF SURFACE SIZING

The chief significance of degree of surface sizing is in relation to writing inks. The suitability of paper for writing must be determined by observation of ink lines and characters on the surface. No method has come into use for expressing this property numerically. Methods which measure the rate of penetration of aqueous solutions into and through paper are not valid for this purpose despite the fact that most of them were proposed with the idea of expressing writing quality numerically. An adequate method giving a numerical expression for degree of surface sizing and applicable to various inks is needed in the interest of research in sizing and in the preparation of specifications of writing papers if not for practical tests. The literature affords no better treatment of testing paper with ink than Herzberg's Papierprüfung.

3. DEGREE OF INTERNAL SIZING

Most uses of paper other than for writing purposes, when the question of sizing is involved at all, demand only resistance to the penetration of aqueous solutions from the surface inward, and writing papers constitute less than 10 per cent of the total output of paper and pulp products. The remainder of this publication will be confined to the consideration of degree of internal sizing toward aqueous solutions.

It is significant that 34 of the 38 methods and modifications which have been described obtain data in terms of penetration into and through the sheet, in spite of the fact that most of them were intended as improved means of testing ink-line resistance. The only possible reconciliation of these various methods involving many different aqueous solutions is on the assumption that the behavior of the solutions is a measure of their common constituent—water. Although this assumption is not valid, it has evidently been tacitly made. That the degree of internal sizing should, in general, be determined by a test of the penetration of water into the sheet is indicated by both the nature of engine sizing and the most common applications of the sizing test. Sizing with rosin consists in changing the highly absorbent fiber surfaces to anticapillary surfaces to prevent wetting and penetration by water and its solutions. There are many uses of paper for which the best available test is for the rate of penetration of water. Such a test appears to be most useful for predicting the probable absorptivity of paper which is to be tub sized, since there is no sensitive indicator or other means of measuring the rate of penetration of the tub-sizing solution as a whole. Moreover, since both the tub-sizing solution and the paper are negative colloids, the selective adsorption (an influence which is discussed later) would be absent

or negligible, making the test with water alone entirely valid. Similarly, paper to be coated should be tested for water penetration, the water, perhaps, being slightly alkaline if a casein coating mixture, which is alkaline, is to be used. In testing such papers as tub sizing, coating, and gumming stock it might be more indicative to test by floating on the solutions or baths to be used with the paper and determining the rate of penetration of the solvent; but the test would still be one of water penetration possibly affected by the dissolved material. These are special problems and could better be worked out in detail by those directly interested. A test of water penetration is the logical procedure, in so far as aqueous liquids are concerned, for paper intended for the lithographic process. In fact, all rosin-sized book papers (if a test for degree of sizing toward aqueous solutions is thought necessary at all) are most satisfactorily tested with water, although the degree of rosin sizing of such papers toward aqueous solutions has no bearing upon their resistance to printing inks. A sizing test of such papers appears to be of value chiefly as an indirect indication of other desirable qualities. The significance of degree of sizing in wrapping papers is in connection with water and moisture resistance. Paper drinking cups obviously are best tested for water resistance. Ice-cream cartons and materials of similar nature which are made into containers for aqueous solutions are preferably tested for resistance to the penetration of water, unless it is possible to devise a special test using the particular aqueous solution in question.

The most generally applicable test capable of giving the most information concerning the internal sizing of paper is resistance to the penetration of water. The work of the Bureau of Standards in connection with testing the degree of sizing of paper has, therefore, up to the present time, been confined almost entirely to the development of adequate methods of testing the rate of penetration of water.

IV. CRITICISM OF METHODS FOR TESTING DEGREE OF INTERNAL SIZING

1. INK TESTS

Observing the behavior of ink lines on the surface of paper is the most rational procedure for testing writing quality. Nevertheless, it is a curious fact that nearly all the sizing tests which use ink depend upon the penetration of the ink through the sheet, as if they were attempts to determine degree of internal sizing instead of writing quality. Experimental evidence shows that, even for estimating the degree of internal sizing, ink-penetration tests are unreliable because of the different manner in which cellulose behaves toward the different substances of which ink is composed. These ink tests depend

upon transudation of the coloring matter; but it has been observed repeatedly that the rate of penetration of the coloring matter of writing ink is not a measure of the rate of penetration of the solvent—water. Hence, a test with ink is not a valid test of the resistance which paper offers to the penetration of water and aqueous solutions other than ink.

Effect of Selective Adsorption from Solution.—One of the characteristic properties of cellulose is its affinity for certain materials in solution, and particularly for colloidally dispersed material which carries a charge opposite to that of cellulose. This affinity is preferential; that is, it is exhibited in different degrees toward different substances. When ink is absorbed by paper, it does not penetrate unchanged, but its several constituents are partially separated and segregated so that the solvent and dissolved materials do not move at the same rate. A part of the material is held back by the affinity of cellulose for it. The segregation of colloidal material is further favored by the increase in concentration of such material as compared to that of the acid which holds it in solution, as a result of which more of the colloidal material agglomerates and goes out of solution. The movement of the solvent is hindered, perhaps mechanically, by the change in effective porosity of the paper as a result of the presence of the agglomerated material. But whatever its mechanism the separation of the dissolved materials within the sheet of paper is an experimental fact, and it is evident that the rate of penetration of the colored materials of the ink is not an indication of the rate of penetration of the solvent, and that the movement of the solvent is influenced by the nature of the dissolved materials and of the affinity of the cellulose for them. This process of selective adsorption is well illustrated by Klemm's absorption test, in which strips of absorbent paper are suspended so that the lower ends dip into an ink bath. As the ink climbs up the strips it is separated into fairly distinct zones of solvent, dye, and suspended matter. In Figure 5 are shown curves obtained by such an absorption test using several solutions which are selectively absorbed by cellulose. The papers used were a mimeograph paper, four blotting papers, and filter paper. The samples are plotted as abscissas and the rise in millimeters in two and one-half minutes as ordinates. It is seen that the solute rises less rapidly than the solvent, the ratio varying for the different solutions and for the different samples. The samples are arranged in the ascending order of their absorptivity toward water, but it is evident that this order is not preserved for the other solutions. This is illustrative of what must occur in the sheet of paper during an ink-penetration test, although the separation of the constituents of the ink can not be readily observed. An ink-penetration test is therefore not indicative of the rate of penetration of any aqueous solution other than ink.

It is difficult to see how the use of the ink flotation test which has been so popular in this country can be justified as a sizing test, since it can not give an adequate measure of either the degree of surface sizing or the degree of internal sizing.

2. METHODS DEPENDING UPON INTERACTING SOLUTIONS

In general, the criticism relative to the effect of selective adsorption applies to this type of test also. One or both of the interacting solutions are usually selectively adsorbed during the time before they meet to produce a color.

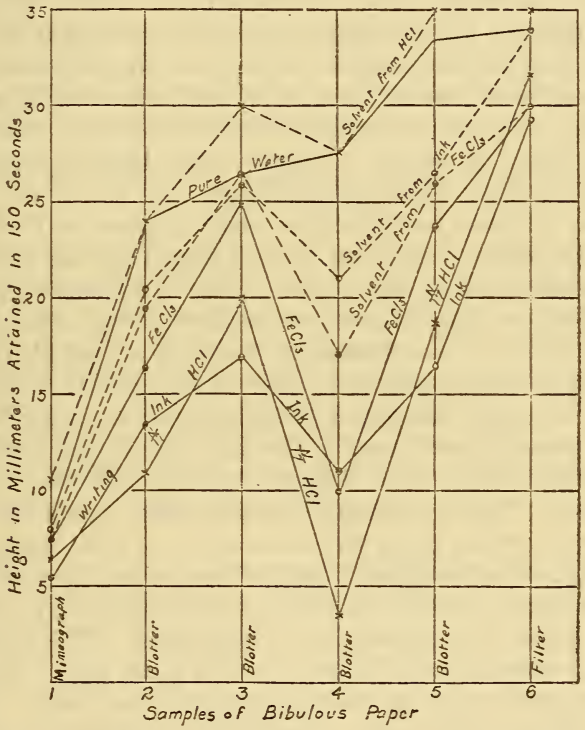

FIG. 5.—*Effect of selective adsorption from solution shown by means of bibulous paper*

The method of Kollmann, in which sodium hydroxide is used, is quite obviously unsuited to the testing of rosin-sized papers for the reason that the rosin is soluble in the sodium hydroxide, and hence is quickly wet through by such a solution even though the paper be well sized.

The best method of this type appears to be that of Stöckigt. The ammonium thiocyanate is apparently not strongly adsorbed by paper, but the ferric chloride, of course, is. It is, perhaps, preferable to carry out the test in a manner similar to the procedure for

the ferrocyanide test; that is, by applying the ferric chloride at intervals always in a new place until the color develops immediately. That this test may sometimes be rather misleading is evident from the behavior of sample D in Figure 7. When considerable ligneous material is present in the paper this test is worthless, since the lignin reduces the ferric chloride and thus delays or entirely prevents the development of the red color.

3. METHODS DEPENDING UPON ELECTROLYTIC CONDUCTIVITY

Since Okell proposed his electrolytic method in 1917 it has received considerable attention and has undergone several modifications. This principle has a rather strong appeal for the reason that the data obtained are of a very positive nature and are reproducible under identical conditions; but this type of test affords an excellent example of the danger of regarding reproducibility of results as the sole criterion of accuracy of results. Besides some minor sources of error, such as incomplete wetting of specimen and the effect of voltage fluctuations in those modifications which dispense with the Wheatstone bridge, there is an error of such magnitude as to prove fatal to the method when applied to the testing of well-sized papers.

Error Due to the Resistance of Entrapped Air.—In a previous publication (4) it was shown, by means of a specially constructed cell capable of being operated at reduced pressure, that the electrical resistance of paper saturated with electrolyte could be reduced greatly in some types of paper if the air was first exhausted from the paper, while in other types of paper exhaustion of the air had little or no effect. The unreasonably high results which are obtained in many cases when using the electrolytic test for sizing are thus easily explained as resulting from the insulating effect of entrapped air. In certain types of paper this air resistance is very large even when the paper is permeated by electrolyte. The air-resistance error is not constant even in paper of the same kind. In papers of different types it may vary several hundred per cent. Thus, it is evident that this test is not a measure of degree of sizing alone but involves a fortuitous error which in many cases more than outweighs the sizing effect on the test results. Some of the factors which appear to influence the air-resistance error are given below.

1. The error appears to be greater the greater the degree of sizing, other things being equal. Hence, the test does not give the proper perspective, but greatly exaggerates the degree of sizing of well-sized papers. This is illustrated by the broken line curve of Figure 9, which has an ever-increasing slope as the degree of sizing of the paper increases.

2. The test seems to be exaggerated also by the porosity of the sheet. A dense paper made from well-beaten stock would give rise

to less error resulting from entrapped air than a porous paper made from free stock. Sizing tests by electrolytic methods on papers made from stock having different degrees of beating are likely to be very deceptive.

3. The electrolytic type of test is influenced by the form and structure of the fibers. Flat ribbonlike fibers with a large specific surface appear to give rise to much higher results by this method than do the round thick-walled fibers. A sulphite bond, for example, usually gives a disproportionately higher "sizing test" by this method than a rag bond.

4. The increase in this "sizing test" with increase of thickness of paper is beyond any reasonable amount. An instance has been observed in which an increase in thickness of 300 per cent during the same machine run resulted in an increase of nearly 13,000 per cent in the test by the electrolytic method.

4. METHODS DESIGNED TO MEASURE THE RATE OF PENETRATION OF WATER

This type of test is best suited to determine the degree of internal sizing of most papers. It is free of the objections which are fatal to the other three types as a means of measuring degree of internal sizing in its relation to most uses of paper; but until recently there has been no satisfactory means of detecting water as it penetrates through paper or of otherwise affording a measure of its rate of penetration. The usual colorimetric reactions with water are not sufficiently sensitive or else can not readily be applied to the detection of water as it penetrates through the sheet from one surface to the other.

The tongue test is, of course, only qualitative and is useful only in getting a rough measure of degree of sizing. Rupture tests are influenced by the structure and formation of the sheet. The method of Herig is an attempt in the right direction, but has not been found sufficiently sensitive. The ground-glass method is very useful when a maximum or a minimum limit can be set for the desired degree of sizing; but this method is of little value when a definite figure is desired. Experimental results indicate that both the curl method and the dry indicator method, as developed at the Bureau of Standards, avoid the above faults and are well adapted to determining the degree of internal sizing of paper.

The curl test is simple, rapid, and reproducible and very useful for testing papers which are relatively thin—those which might be called the creasing or folding type. This test can be carried out with simple apparatus, but is most conveniently made with apparatus of the type shown in Figure 3 and described in a previous publication (6).

The Bureau of Standards new method using a dry indicator for water is the most generally applicable test of this type. It avoids the effect of selective adsportion by applying a dry indicator to the upper side of paper floated on water, the indicator being sensitive to water and readily revealing that which penetrates through the sheet. The development of the color of the dye gives a fairly sharp end point when using very soluble dyes in a highly soluble diluent, such as pulverized sugar. The apparatus required is simple; the test is comparatively rapid and, in general, very satisfactory.

Factors Requiring Additional Investigation.—Attempts to make correction for difference in thickness of samples of paper tested for relative degrees of sizing have, in general, not been satisfactory. In the description of some methods it is recommended that the time of the test be divided by the weight of the sample per ream or per square meter in order to obtain comparative figures. This recommended procedure is apparently not founded on any rational ground, but assumes the rate of penetration to be uniform and the time of transudation proportional to the thickness of the sheet and the thickness in turn to be proportional to the weight of the sheet. These assumptions are entirely erroneous. Consideration of the laws of capillary dynamics leads to the conclusion that the time required for water to penetrate through paper is approximately proportional to the square of the thickness of the sheet. Consistent results in testing samples of different weights and thicknesses have been obtained by dividing the time in seconds of the sizing test, obtained with either the curl method or the dry-indicator method, by the square of the thickness in mils of the paper and using the quotients as comparative figures of degree of internal sizing.

Comparative tests by the Bureau of Standards methods should be made at a constant temperature and a fairly uniform relative humidity. It has been definitely shown that the tests are affected by changes in relative humidity; but the effects of different temperatures and humidities and the precise relation between the test time and the thickness of the papers tested are problems which will require considerable additional investigation.

V. COMPARISON OF THE OUTSTANDING METHODS IN DETERMINING THE DEGREE OF INTERNAL SIZING OF PAPER

1. NATURE OF THE COMPARATIVE STUDY

The outstanding methods of each of the four types which have been discussed were selected for comparative tests. From the first group the ink-flotation method was chosen, since this method is widely used in this country and enjoys the sanction of precedent.

From the second group the Stöckigt method was selected, since this method appears to be the best of its type and is used to a considerable extent. From the third group the Boon and Fourness modification was chosen for most of the tests, since a well-known commercial instrument employs this modification of the electrolytic type of testing method. This tester is referred to hereafter in this publication as B and F electrolytic (Type II in the figures). The Bureau of Standards modification, which is referred to hereafter as B. S. electrolytic (Type I in the figures), was used in a series of comparative tests with the B and F electrolytic and in the tests represented in Figure 7. In comparing these two types of the electrolytic method it was found that under the same conditions the two correspond very closely, provided at least 10 tests were made on each sample, although there is a greater variation among the individual tests in the case of the B and F electrolytic method. The graphs of Figure 6 illustrate the degree of correspondence of the two modifications when the tests are made under identical conditions. From the fourth group the curl method and the dry-indicator method were selected, since these methods have proved to be the best of this type.

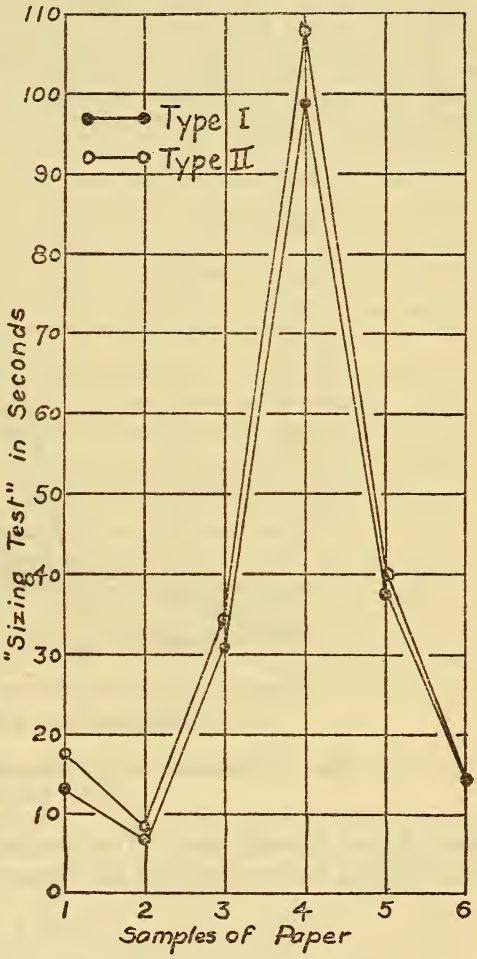

FIG. 6.—*Comparison of Types I and II of the electrolytic sizing test method*

In these tests no attempt was made to correct the data for differences in thickness of the papers tested and obtain an absolute figure for degree of sizing. The experimental data (time in seconds) were plotted against the various samples of paper tested, the time of test serving as well as the absolute values for the purpose of comparing the several methods.

2. COMPARATIVE STUDY USING PAPERS OF DISSIMILAR CHARACTER

For this comparison six samples of paper of different character as tabulated in Table 1 were selected. Ten specimens were prepared from each sample for each testing method. All the tests were made in one day in order to obviate any possible discrepancies which might be due to different testing conditions. In Figure 7 the results of the test (time in seconds) are plotted as ordinates and the samples as abscissas, each point representing the average of 10 tests. In order to bring the curves together for ready comparison, it was necessary to multiply the results of three of the methods by a constant factor in each case. The curl data were multiplied by three, the Stöckigt by two, and the ink-flotation by one-fourth.

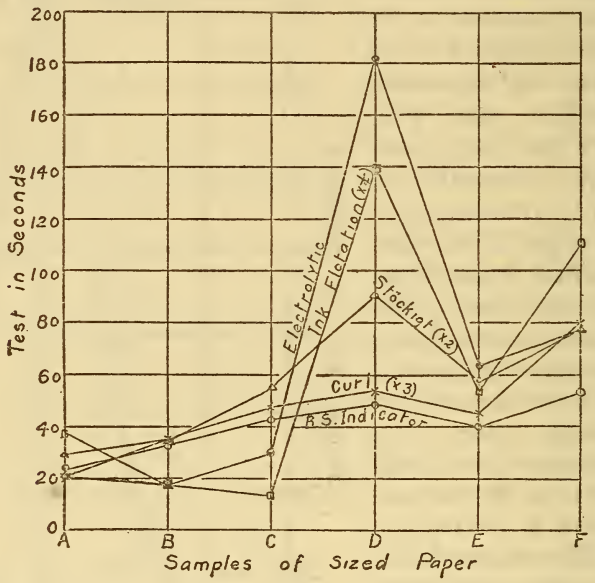

FIG. 7.—*Comparison of sizing test methods using dissimilar papers*

TABLE 1

Sample	Kind	Weight 25 by 40 inches 500 sheets	Thickness	Ash	Rosin	Fiber composition	
						Rag	Bleached chemical wood
		Pounds	*Mils*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
A	Book	42	3.7	0.7	1.1	50	50
B	do	54	2.9	9.6	1.4	----------	100
C	do	72	4.4	24.4	1.0	----------	100
D	Writing	54	3.4	2.9	2.2	----------	100
E	do	47	2.6	8.1	1.9	----------	100
F	Bond	69	4.1	.2	1.0	100	----------

If the fact is kept in mind that the values plotted for the ink-flotation test are but one-fourth the actual values, and that the solutions penetrate from both sides at once in the Stöckigt and electrolytic method, the effects of adsorption from solution and of the resistivity error are evident. The effect is especially marked in the case of sample D, which is a hard sized writing paper made of wood fiber. The sizing test is exaggerated to many times its real value. At first glance the electrolytic and ink flotation methods appear to be in good agreement; but they agree only in that both give very high values for sample D. They are badly reversed for most of the other samples. The curl and dry indicator methods are the only ones which show close agreement. The curl test for sample F is too high, and the agreement is not so good in this case. The reversal of curling was hard to determine on this sample, as it exhibited a series of false reversals in the neighborhood of the critical point. The data for the Stöckigt method is fairly consistent but shows an ever-increasing error as the values increase.

It will be observed that the results obtained by the curl and dry indicator methods do not cover a very wide range of values. This has been the chief criticism which the methods have encountered. The situation involves a subtle psychological element which demands that any new method shall give results comparable to those obtained with the ink-flotation test or some other time-honored test. The answer to the criticism, of course, is that these customary methods involve characteristic errors which have already been discussed and which give exaggerated and illusory values as the higher values are approached, while the curl and dry indicator methods give real comparative values of resistance to wetting. There is no attempt to reconcile these two methods with the older tests.

3. COMPARATIVE STUDY USING PAPERS OF SIMILAR CHARACTER

In this series of tests 57 samples of medium to hard-sized book paper made in the Bureau of Standards experimental paper mill were used. These 57 samples were all made on the same paper machine and from the same stock and as nearly as possible alike except for their content of sizing and loading materials. The stock consisted of soda and sulphite pulps in equal proportions. The amount of rosin and the kind and amount of filler contained in each paper is given in connection with the graphs of Figure 8, which shows the results of this comparison. In this figure the samples are grouped according to the kind of filler used except the last group in which glue has been added to the beater, and in each group the attempt was made to arrange the samples in the order of decreasing rosin content and increasing filler content, bearing in mind that a large increase in filler content has more effect on the degree of sizing

than a small decrease in rosin content; that is, the samples in each group were arranged as nearly as possible in the decreasing order of the anticipated degree of sizing. The ink-flotation data were so

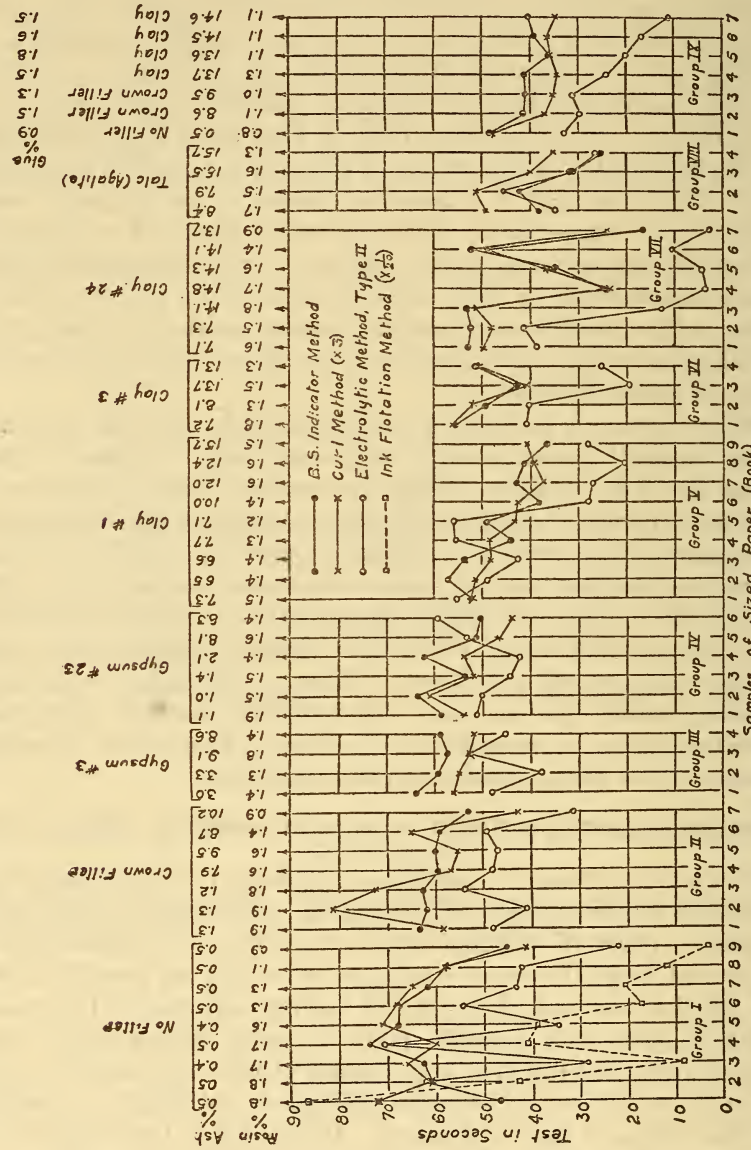

FIG. 8.—*Comparison of sizing test methods using similar papers*

high that it was necessary to divide each value by 20 in order to plot them with the other data. The results by this method seemed so fruitless that the tests were discontinued after the first group. In

Figure 9 the data obtained with the curl and electrolytic methods on all samples represented in Figures 7 and 8 are plotted against the corresponding data obtained with the dry-indicator method, agreement, of course, being indicated by the proximity of the points to a straight line. The very high point of Figure 7 was omitted, since it would require undesirable extension of the graph. It is seen that the electrolytic data do not readily form any smooth curve, but are grouped best about a curve shown by the broken line which has an ever increasing slope. The curl data, on the other hand, lie, in general, close to a straight line.

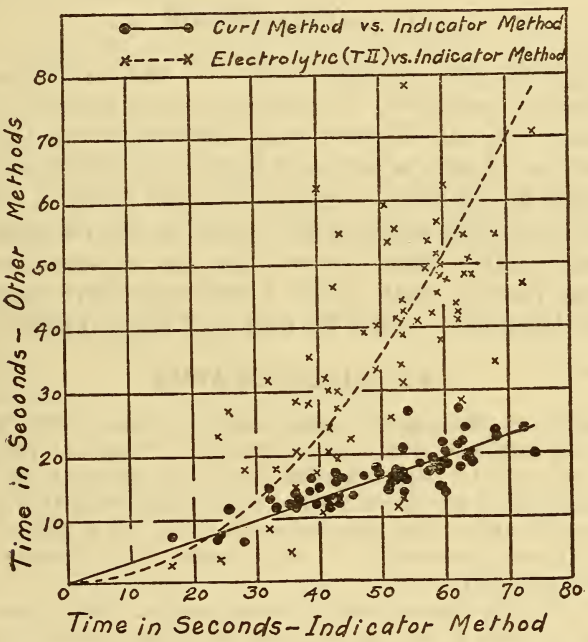

FIG. 9.—*Curl method and electrolytic method plotted against the dry-indicator method of testing paper sizing*

From the data presented in the above graphs it may be concluded that:

(*a*) The most probable relative degrees of internal sizing of the various samples are best represented by the data of the Bureau of Standards dry-indicator method.

(*b*) The agreement of the curl method with the dry-indicator method is, with a few exceptions, very good.

(*c*) The Stöckigt method gives fairly consistent results, but is characterized by an error which increases with increase of degree of sizing, the error being due presumably to the influence of selective adsorption.

(*d*) The data obtained with the electrolytic method are, in general, too erratic and inconsistent to be of much value in appraising paper for degree of sizing. In some cases this method agrees satisfactorily with the methods which measure the rate of penetration of water, but the degree of concordance does not follow any clearly defined principle, and hence the method can not be depended upon for consistent results.

(*e*) The ink-flotation test is too erratic and fruitless of useful information to be considered seriously as a test of the degree of internal sizing of well-sized papers.

VI. CONCLUSIONS

1. Of the four types of sizing tests—(*a*) tests with ink, (*b*) tests using interacting solutions, (*c*) tests using the principle of electrolytic conductivity, and (*d*) tests with water—the first three involve inherent sources of error which, to a large extent, invalidate methods of these types in testing the degree of internal sizing of paper. The fourth type, tests with water, is best suited to the purpose.

2. Experimental evidence shows that the dry-indicator method and the curl method, both of the fourth type, give the most consistent and dependable values for degree of internal sizing.

VII. BIBLIOGRAPHY

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